

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-119204

(43)Date of publication of application : 23.04.2003

(51)Int.Cl.

C08F 2/26

C08F 14/18

C08F 16/24

(21)Application number : 2001-309905

(71)Applicant : DAIKIN IND LTD

(22)Date of filing : 05.10.2001

(72)Inventor : HOMOTO YUKIO  
NEGISHI YOSHIO  
MORIMOTO KAZUYOSHI

## (54) METHOD FOR MANUFACTURING FLUORINE-CONTAINING POLYMER LATEX

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for manufacturing a fluorine-containing polymer latex for furnishing a fluorine-containing polymeric material having excellent powder properties and mechanical properties when molded that are comparable with those of the conventional materials.

SOLUTION: This fluorine-containing polymer latex is manufactured by subjecting to emulsion polymerization in an aqueous medium, a single fluorine-containing olefin, or a fluorine-containing olefin and another monomer, in the presence of at least one type of fluorine-containing surfactant represented by formula (I):  $Rf_1O(CFX-CF_2O)_p-CFX-COOM$ , formula (II):  $Rf_2OCF_2(CH_2)_nO(CFX-CF_2O)_p-CFX-COOM$ , formula (III):  $M_1OCO(CF_2)_mCOOM_2$ , or formula (IV):  $Rf_3(CH_2)_nOCO-CH(SO_3M)-CH_2-COO(CH_2)_n'Rf_3'$ , (wherein  $Rf_1$  is a 1-5C perfluoroalkyl group;  $Rf_2$  is a 2-3C alkyl group other than a perfluoroalkyl group that contains one or more fluorine atom;  $Rf_3$  and  $Rf_3'$  are, the same or different, a 1-4C alkyl group having one or more fluorine atom; and X is a fluorine atom, a chlorine atom, or a 1-4C perfluoroalkyl group).

## LEGAL STATUS

[Date of request for examination] 24.08.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

• NOTICES •

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.  
2. \*\*\* shows the word which can not be translated.  
3. In the drawings, any words are not translated.

## CLAIMS

**[Claim(s)]**

(Claim 1) (Formula I): R(O(GFX-CF2O)<sub>n</sub>-p-GFX-COOM (among a formula) R11 — perfluoroalkyl radical [of carbon numbers 1-5]; X — a fluorine atom — integer; M of 0-5 perfluoroalkyl radical of a chlorine atom or carbon numbers 1-4 hydrogen atom, the fluorine-containing surfactant with which it is expressed by ammonium, the alkali-metal atom, or the alkaline-earth-metal atom (I), Formula (II): R12(CF3-CH2)<sub>2</sub>n(GFX-CF2O)<sub>p</sub>-p-GFX-COOM (among a formula) alkyl group [of the carbon numbers 2 or 3 whose R2 is not or more 1 hidden perfluoro onto a fluorine atom]; — n — integer [of 1-3]; X — a fluorine atom — integer; M of 0-5 perfluoroalkyl radical of a chlorine atom or carbon numbers 1-4 hydrogen atom, the fluorine-containing surfactant with which it is expressed by ammonium, the alkali-metal atom, or the alkaline-earth-metal atom (II), Formula (III): M1OCO (CF2)<sub>m</sub>mCOOM2 (as for m, integer; M of 2-4 and M2 are a hydrogen atom, ammonium, an alkali-metal atom, or an alkaline-earth-metal atom among a formula) even when it is the same — differing — — — — the fluorine-containing surfactant (III) with which it is expressed — Or formula (IV): R13(CF3-CH2)<sub>2</sub>nOCO-CH(SO3M)-CH2-COOCH2 n'R13' (R13 and R13' are the alkyl groups of the carbon numbers 1-4 containing one or more fluorine atoms among a formula) The same n and n' which may differ but becomes independent. Integer; M of 1-3 A hydrogen atom, Under at least one sort of a fluorine-containing surfactant (IV) of existences expressed by ammonium, the alkali-metal atom, or the alkaline-earth-metal atom, in an aqueous medium The manufacture approach of the fluorine polymer latex which is fluorine-containing olefin independent or is characterized by carrying out the emulsion polymerization of a fluorine-containing olefin and other monomers.

[Claim 2] Said fluorine-containing surfactant (I) CF<sub>3</sub>OCF<sub>2</sub>OCF(CF<sub>3</sub>)COONH<sub>4</sub>, CF<sub>3</sub>OCF(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)COONH<sub>4</sub>, CF<sub>3</sub>CF<sub>2</sub>OCF(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)COONH<sub>4</sub>, CF<sub>3</sub>CF<sub>2</sub>OCF(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)COONH<sub>4</sub>, CF<sub>3</sub>CF<sub>2</sub>OCF(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)COONH<sub>4</sub>, CF<sub>3</sub>CF<sub>2</sub>OCF(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)COONH<sub>4</sub>, CF<sub>3</sub>CF<sub>2</sub>OCF(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)COONH<sub>4</sub>, CF<sub>3</sub>CF<sub>2</sub>OCF(CF<sub>3</sub>)CF<sub>2</sub>OCF(CF<sub>3</sub>)COONH<sub>4</sub>, or the manufacture approach according to claim 1 which is one sort of CF<sub>3</sub>CF<sub>2</sub>OCF<sub>2</sub>CF<sub>2</sub>OCF(CF<sub>3</sub>)COONH<sub>4</sub>, or two sorts or more.

[Claim 3] The manufacture approach according to claim 1 that said fluorine-containing surfactant (II) is  $\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OCF}(\text{CF}_3)\text{COONH}_4$ .

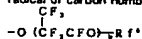
[Claim 4] The manufacture approach according to claim 1 that said fluorine-containing surfactant (III) is  $\text{H}_4\text{NOCO}(\text{CF}_2\text{CF}_2)_2\text{COONH}_4$ .

[Claim 5] The fluorine-containing surfactant (IV) is H(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>COOCH<sub>2</sub>(SO<sub>3</sub>NH<sub>4</sub>) CH<sub>2</sub>COOCH<sub>2</sub>(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>H or H(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>COOCH<sub>2</sub>(SO<sub>3</sub>Na) CH<sub>2</sub>COOCH<sub>2</sub>(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>H.

[Claim 6] said fluorine-containing olefin — formula (1): — [Formula 1]



For the inside of [type, and Y1, F, Cl, H, or CF<sub>3</sub>; Y2 are F, Cl, H, Rf5 (Rf5 is the perfluoroalkyl radical of carbon numbers 1-10), or [Formula 2].



The monomer shown by, or a formula (2) (Rf8 is the perfluoroalkyl radical of carbon numbers 1-6, and b is the integer of 0, or 1-5) [Formula 3]



(-- the manufacture approach according to claim 1 to 5 that the inside of a formula and Z1 are one sort of the monomer perfluoroalkyl radical: Z2 of the alkyl group of F, H, and carbon numbers 1-6 or carbon numbers 1-10 are indicated to be by the alkyl group of H, Cl, and carbon numbers 1-6, or  $-(CF_2)_d$ -Z3(d is integer of 1-10 and Z3 is F or H), or two sorts or more.

[Claim 7] The manufacture approach according to claim 6 that said fluorine-containing olefin is a par halo olefin Y1 and whose Y2 are either F, Cl or Rf5 in a formula (1).

(Claim 8) The manufacture approach according to claim 7 that said par halo olefin is tetrafluoroethylene, perfluoro (alkyl vinyl ether), hexafluoroisopropylene, or chlorotrifluoroethylene.

[Claim 9] The manufacture approach according to claim 8 that said fluorine-containing olefin is vinylidene fluoride each of Z1 and whose Z2 is F in a formula (2)

vinylidene fluoride each of Z1 and whose Z2 is F in a formula (2).

[Claim 10] said — others — the manufacture approach according to claim 1 to 9 that a monomer is one sort of the ethylenic unsaturated monomer of a non-fluorine system, or two sorts or more.

[Claim 11] The manufacture approach according to claim 1 to 7 that the fluorine polymer obtained is a par halo polymer.

[Claim 12] or [that said par halo polymer has denaturalized] — or the manufacture approach according to claim 11 which is the polytetrafluoroethylene which is not carried out a

According to claim 11 which is the polytetrafluoroethylene which is not carried out, a tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-perfluoro (alkyl vinyl ether) copolymer, or polychlorotrifluoroethylene resin.

[Claim 13] The manufacture approach according to claim 1 to 7 that the fluorine polymer obtained is a non-par halo polymer.

[Claim 14] Said norborn base polymer The homopolymer of vinylidene fluoride, trifluoro ethylene, or vinyl fluoride, or these two or more sorts of copolymer; tetrafluoroethylenes, Perfluoro (alkyl vinyl ether), hexafluoropropylene, or chlorotrifluoroethylene and vinylidene fluoride, Two or more sorts of copolymer; or tetrafluoroethylenes of trifluoro ethylene and vinyl fluoride, 2, 3, 3, 4, 4 and 5, 5-heptafluoro-1-pentene or 3 and 3, and a 3-trifluoro-2-(trifluoromethyl) and vinylidene fluoride, Perfluoro (alkyl vinyl ether), hexafluoropropylene, Chlorotrifluoroethylene and vinylidene fluoride, trifluoro ethylene, One sort or two sorts or more, and ethylene of vinyl fluoride, 2, 3, 3, 4, 4 and 5, 5-heptafluoro-1-pentene or 3 and 3, and a 3-trifluoro-2-(trifluoromethyl)-1-propene, The manufacture approach according to claim 13 which are one sort of a propylene, vinyl ether, vinyl ester, or acrylate, or two sorts or more of copolymers.

**Claim 15]** The manufacture approach according to claim 1 to 14 which adds at least one sort of a fluorine-containing surfactant according to claim 1 to 5 in 0.001 – 15.0% of the weight of an amount to an aqueous medium at the time of polymerization initiation, and starts an emulsion polymerization.

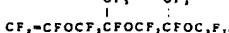
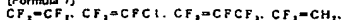
[Translation done.]



[0041] As a fluorine-containing olefin which is the monomer which carries out a polymerization, the monomer shown by said formula (1) or formula (2) is raised with the manufacture approach of this invention, and a polymerization is presented with 1 of sorts of these, and two sorts or more.

[0042] As an example of the monomer shown by the formula (1), it is [0043].

[Formula 7]



[0044]  $CF_2=CF_2$  is raised preferably.

[0045] Perfluoroolefins and chlorotrifluoroethylenes (CTFE), such as par halo olefins (TFE), for example, tetrafluoroethylene, hexafluoropropylene (HFP), and perfluoro (alkyl vinyl ether), are especially desirable.

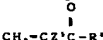
[0046] As an example of the monomer shown by the formula (2),  $CH_2=CHF$ ,  $CH_2=CF_2$ ,  $CH_2=CFCH_3$ ,  $CH_2=CF(CF_3)$ ,  $CH_2=CHCF_2CF_3$ ,  $CH_2=CF(CF_2CF_3)$ , etc. can be raised preferably, for example. The vinylidene fluoride especially shown by  $CH_2=CF_2$  is desirable.

[0047] In this invention, these fluorine-containing olefins can be homopolymerized, or fluorine-containing olefins can be copolymerized, and it can copolymerize with the ethylenic unsaturated monomer of a non-fluorine system further.

[0048] As an ethylene nature partial saturation non-fluorine monomer, for example Ethylene, a propylene, isobutene and a formula:  $CH_2=CH-O-(C=O)-R^1$  (among a formula) R7 The aliphatic series radical of carbon numbers 1-17, the alicyclic radical of carbon numbers 3-17, the fluoro alkyl group of carbon numbers 1-20. The alkyl vinyl ether or vinyl ester shown is raised.  $R^1 = -O$  or  $-I$  — it is — as an example For example, the methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether, isopropyl vinyl ether, n-butyl vinyl ether, isobutyl vinyl ether, Cyclohexyl vinyl ether, 2 and 2, 2-trifluoroethyl vinyl ether, 2, 2, 3, and 3-tetrafluoro propyl vinyl ether, 2, 2, 3 and 3, 3-pentafluoro propyl vinyl ether, Acetic acid vinyl ester, propionic acid vinyl ester, butanoic acid vinyl ester, pivalic acid vinyl ester, BASA tic acid vinyl ester, cyclohexane-carboxylic acid vinyl ester, etc. are raised.

[0049] Furthermore, it is formula: [0050].

[Formula 8]



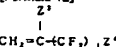
[0051] the inside of a formula, and Z5 — H, Cl, F, CH3, and CF3; R8 — H, Cl, and F — The compound expressed with the aliphatic series radical of carbon numbers 1-17, the alicyclic radical of carbon numbers 3-17, or the fluoro alkyl group of carbon numbers 1-20 is raised. As an example isobutyl acrylate, methyl acrylate, ethyl methacrylate, 2, 2, 3, 3, and 3-pentafluoro propyl-alpha-fluoro acrylate, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, and 7-dodeca fluoro penta-alpha-trifluoromethyl acrylate, Cyclohexyl acrylate, 2, 2, 3, 3, 4, 4, 5, 5, 6, 6, 7, 7, 8, 8, 9, 9, 10, 10, 11, 12, 12, 13, 13, 14, 14, 15 and 15, and 15-nonacos fluoro penta-decyl acrylate, Octyl-alpha-chloro acrylate, octadecyl acrylate, etc. are raised.

[0052] Moreover, the compound shown by formula:  $CH_2=CHCH_2Z^6$  (Z6 shows the alkoxy group of a chlorine atom or carbon numbers 1-8 among a formula) can also be used, and an allyl

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\_web.cgi.eje

2006/06/19

[Formula 12]

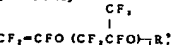


[0068] The hexafluoro isobutylene as the above with (same) Z3, Z4, and i.e. is desirable.

[0069] One of the copolymers of the shape of an elastomer which uses TFE as a principal component is a copolymer with which TFE consists of 40-70-mol % and 30-60 mol % of propylenes [i.e. moreover — these — others — a copolymerizable component, for example, VdF and HFP, CTFE, and perfluoro vinyl ether — less than [40 mol %] — it can also contain.

[0070] Another elastomer-like polymer is a polymer which consists of TFE and perfluoro vinyl ether, and is 40-85 mol % and type: [0071]. [of TFE(a)]

[Formula 13]



[0072] Perfluoroalkyl radical of carbon numbers 1-8 is shown by integer of 0, or 1-5, and (type Naka and R9 are perfluoro vinyl ether 15 - 50-mol % of a polymer.

[0073] The 2nd group of a desirable fluorine polymer which manufactures by the manufacture approach of this invention is a polymer which uses VdF as a principal component.

[0074] namely, the copolymer obtained by using VdF as an indispensable component and copolymerizing other monomers if needed further — it is — VdF — more than 40 mol % — it is the fluorine polymer to contain.

[0075] In this VdF system polymer, TFE, CTFE, HFP, hexafluoro isobutene, and perfluoro vinyl ether are desirable examples as other copolymerizable monomers.

[0076] As an example of the fluorine polymer which uses VdF as a principal component, the homopolymer (PvDF) of VdF, the copolymer of VdF and TFE, the copolymer of VdF and HFP, the copolymer of VdF and TFE and HFP, the copolymer of VdF, TFE, and CTFE, the copolymer of VdF, TFE, and CF3 OCF=CF2, etc. are raised preferably.

[0077] Moreover, these fluorine polymers that use VdF as a principal component can be used as the polymer of the shape of the shape of resin, and an elastomer by choosing various other existence, classes, and presentation ratios of a monomer component to copolymerize.

[0078] As an example of the VdF system polymer of the shape of desirable resin, a VdF/TFE (50 - 99 / 1-50-mol ratio (%)) copolymer, a VdF/TFE/HFP (% 45 - 99/0 - 45 / 1-10-mol ratio) copolymer, a VdF/TFE/CTFE (% 50 - 99/0 - 30 / 1-20-mol ratio) copolymer, VdF/TFE/HFP (% 45 - 99/0 - 45 / 1-15-mol ratio), etc. are raised also in it.

[0079] Moreover, as an example of the presentation range which becomes elastomer-like, 40-85-mol % and TFE are raised for VdF, and 15-50-mol % of a copolymer is preferably raised with a VdF system copolymer for 0-30-mol % and HFP.

[0080] Furthermore, a fluorine-containing segmentation polymer which is indicated by JP.81-49327.B is also contained as an example of a fluorine polymer.

[0081] It intervenes between the residue except this iodine atom, and this iodine atom and this residue, and if few, it will become this fluorine-containing segmentation polymer from the iodine atom isolated from the iodine compound which has fundamentally the iodine atom combined with the carbon atom, and this iodine compound considering two sorts of polymer chain segments (however, at least one of sorts [them] is a fluorine-containing polymer chain segment) as an indispensable constituent. If it puts in another way, the fluorine-containing segmentation polymer of this invention will become fundamentally considering the residue excluding this iodine atom from the iodine atom isolated from the iodine compound which has the iodine atom combined with the chain which consists of at least two sorts of polymer chain segments (however, at least one of sorts [them] is a fluorine-containing polymer chain segment), and the carbon atom which exists in the both ends, and this iodine compound as a part for an indispensable configuration, namely, the typical structure of a fluorine-containing segmentation polymer —

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\_web.cgi.eje

2006/06/19

chloride, allyl compound methyl ether, allyl compound isopropyl ether, the allyl compound octyl ether, etc. are raised as an example.

[0053] Moreover, in addition to this, styrene and a styrene derivative, and maleic-acid dialkyl ester are raised.

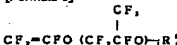
[0054] The non-fluorine monomer of fluorine-containing  $CF_2=CF_2$  which has functional groups given in WO 95/No. 33782 pamphlet, such as a hydroxyl group, a carboxyl group, a carboxylate radical, an epoxy group, and a thiol group, is also copolymerizable further again.

[0055] The desirable structure of the fluorine polymer obtained by this invention can be divided roughly into two, what uses tetrafluoroethylene (TFE), hexafluoropropylene (HFP), or chlorotrifluoroethylene (CTFE) as a principal component as a fluorine-containing olefin, and the thing which uses vinylidene fluoride (VdF) as a principal component.

[0056] That is, the 1st group is a fluorine polymer which uses TFE, HFP, or CTFE as an indispensable component, copolymerizes a copolymerizable monomer besides the above if needed further, and is obtained.

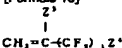
[0057] Setting to the aforementioned polymer, especially a desirable thing is VdF, hexafluoropropylene (HFP), hexafluoro isobutene, and formula: [0058] as other copolymerizable monomers.

[Formula 9]



[0059] For perfluoroalkyl radical of carbon numbers 1-8, (type Naka and R9 are the perfluoro vinyl ether shown by integer) of 0, or 1-5, and formula: [0060].

[Formula 10]



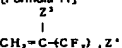
[0061] H or F; Z4 has [ (type Naka and Z3) the fluorine-containing olefin and ethylene in which H or F is shown by integer) of 1-10, a propylene, 1-butene, desirable isobutene, etc.

[0062] As a still more detailed example of the fluorine polymer which uses TFE, HFP, or CTFE as a principal component The homopolymer (PTFE) of TFE, the homopolymer of CTFE (PCTFE). The copolymer (FEP) of TFE and HFP, the copolymer of TFE and perfluoro vinyl ether (less than [10 mol %]) (PFA), It responds to TFE or CTFE, ethylene, and a pan at the need. A copolymer with a copolymerizable fluorine-containing olefin (E (C) TFE), HFP, ethylene, the copolymer of the shape of an elastomer which copolymerized TFE depending on the case. The copolymer of the shape of an elastomer which copolymerized TFE, the copolymer of the shape of an elastomer which copolymerized the propylene and TFE, and perfluoro vinyl ether (more than 15 mol %) etc. is raised preferably.

[0063] 0.3-5.0 mol % of the copolymer of perfluoro vinyl ether indicated in detail to be 95-99.7 mol % of TFE(s) as a PFA system copolymer in the inside of it by formula:  $CF_2=CFORF10$  (the inside of a formula and R10 are the perfluoroalkyl radical of carbon numbers 1-8) is desirable.

[0064] Moreover, as an (EC) TFE system copolymer, the fluorine-containing olefin 0 of the 3rd component used TFE or CTFE30 70-mol % and ethylene 30 - if needed [70 mol % / % and if needed] - 15-mol % of a copolymer are desirable. As a fluorine-containing olefin as the 3rd component, it is [0065].

[Formula 11]



[0066] (type Naka and Z3 can use the fluorine-containing olefin shown by integer) of 1-10, perfluoro vinyl ether, HFP, a hexafluoro isobutylene, etc., and H or F; Z4 is [H or F] [0067] especially.

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\_web.cgi.eje

2006/06/19

degree type-Q- [(A-B-...) ] — among [type F' The residue except an iodine atom, A and B. .... O from an iodine compound, respectively A polymer chain segment (it corrects and at least one of them is a fluorine-containing polymer chain segment), the iodine atom with which I was isolated from said iodine compound, and f' can be expressed with] showing the number of the joint hands of Q.

[0082] Especially or more 5000 extent is [2000 or more] usually desirable [for a shaping application / generally / from the point of the own mechanical strength of a fluorine polymer / that it is not much low], for example, although suitable range especially differs and the molecular weight of the fluorine polymer obtained by this invention is not limited by the class of polymer, an application, and operation as number average molecular weight preferably. Moreover, especially or less 750000 extent is [1 million or less] usually preferably desirable [that it is not much high] from the point of a moldability.

[0083] The copolymer of the shape of resin which uses above TFE as a principal component in the example of a fluorine polymer further again. For example, when it is the fluorine polymer in which melting processing like PFA, FEP, and ETFE is possible, The melt flow value is the measurement temperature (for example, it PFA(s)) defined depending on the class of fluorine polymer. In FEP, it sets at 372 degrees C, and sets against 300 degrees C and a load (for example, 7kg) in ETFE, 0.01x10<sup>-2</sup> - 50x10<sup>-2</sup> ml/sec. It is 0.1x10<sup>-2</sup> - 10x10<sup>-2</sup> ml/sec. preferably [it is desirable and] to 0.05x10<sup>-2</sup> - 25x10<sup>-2</sup> ml/sec. and profit.

[0084] moreover, the case of a fluorine polymer meltable to solvents, such as DMF, such as a polymer of the shape of the shape of resin which consists of one or more sorts of the polymer of the shape of an elastomer which uses TFE or HFP as a principal component, the homopolymer of VdF and VdF, TFE and HFP, or CTFE, and an elastomer, and THF, for example, the determination-of-molecular-weight value of the polystyrene conversion by GPC, — it is — number average molecular weight — 2000-1 million — desirable — 5000-750000 — it is the thing of 10000-500000 especially preferably.

[0085] Moreover, in the case of the homopolymer (PTFE) of TFE, with a molecular weight of about 2000 to 1 million currently called the common-name low molecular weight PTFE from the oligomer-like thing thing and the high molecular weight object which cannot carry out melting processing further are included. The molecular weight in the case of the amount PTFE of macromolecules can be manufactured to what is 1 million-10 million, and a maximum of 20 million about about, although it cannot specify.

[0086] The fluorine polymer latex of this invention is manufactured by the emulsion-polymerization method. Hereafter, first, polymerization conditions, an additive, etc. about a fluorine polymer at large are explained, and the suitable surfactant for each, polymerization conditions, an additive, etc. are explained for every fluorine polymer typical subsequently.

[0087] As an initiator used by the emulsion polymerization, although the usual radical initiator can be used A water-soluble initiator is adopted preferably. Specifically Perosulfuric acid, hydrogen peroxides, such as an ammonium persulfate salt, organic peroxide (diisopropyl peroxy dicarbonate and di-n-propyl peroxy dicarbonate —), or these and sodium hydrogensulfates, such as t-butylperoxy persulfate. The redox initiator which consists of combination with reducing agents, such as a sodium thiosulfate and a hydroxy methane sulfonic acid; Still a small amount of iron to these. Dibasic-acid peroxides, such as inorganic system initiator [of the system which made ferrous salt, silver sulfate, etc. live together], or disuccinic acid peroxide, and azoguru tar-acid peroxide; azobis isobutyl amine dihydrochloride etc. is raised. Moreover, the azo compound of water-soluble or oil solubility can be used similarly.

[0088] The description of this invention is that it uses the fluorine-containing surfactant of said formula (I) - (IV) as a surfactant at the time of an emulsion polymerization (emulsifier). The amount used is about 0.01 - 10 % of the weight preferably 0.001 to 20 % of the weight in a sum total addition to a polymerization solvent (aqueous medium).

[0089] Furthermore, a well-known chain transfer agent, a buffer for pH, pH regulator, etc. can also be used if needed.

[0090] As a chain transfer agent, an isopentane, a diethyl malonate, ethyl acetate, n-hexane, a cyclohexane, a methanol, ethanol, a tert-butanol, a carbon tetrachloride, chloroform, a methylene

http://www4.ipdl.ncipi.go.jp/cgi-bin/tran\_web.cgi.eje

2006/06/19





[0176] Perfluoro adipic acid 2, ammonium 182g (0.50 mola) was obtained by adding 63g (1.04 mola) of aqueous ammonia, and 100g of water to 150g (0.517 mola) of synthetic ester 3, perfluoro adipic acid 28%, and removing water by distillation, 97% yield.

[0177] When the surface tension of the water solution of this ammonium salt was measured, by 10 mass % concentration, 65.5 mN/m, therefore critical micelle concentration were not measured by 69.6 mN/m and 0.1 mass % concentration with 47.8 mN/m and 1 mass % concentration, and were not measured by 87.6 mN/m and 0.001 mass % concentration with 70.8 mN/m and 0.01 mass % concentration. The melting point T<sub>g</sub>/DTA measurement of this ammonium salt was [ 260 degrees C and 50% decomposition temperature of 147 degrees C and 10% decomposition temperature ] 280 degrees C.

[0178] The boiling reflux of the synthetic examples 42, 2, 3, 1, 4, 4, and 5, 5-octafluoro-1-pentanol 116g (0.50 mola) and 23.5g (0.24 mola) of maleic anhydrides, and the 9.5g (0.05 mola) of the p-toluenesulfonic acid monohydrates is carried out in 1 l of toluene, and the separating water was removed with azeotropy. Afterbaking was stopped for 21 hours and it washed in cold water at 70 degrees C. By carrying out reduced pressure Shimo fractional distillation of the toluene layer, 103g (2, 2, 3, 1, 4, 4, 5, and 5-octafluoro-1-pentyl) (0.19 mola) of maleic-acid screws was obtained. 1 H-NMR(THF- $\delta$ ): 6.13 (t, 2H, HC<sub>2</sub>F2) delta.4.74 (t, 4H, CH<sub>2</sub>O), 6.41 (s, 2H, CH=),

[0179] The solution which melted maleic-acid bis(2, 2, 3, 1, 4, 4, 5, and 5-octafluoro-1-pentyl) 50.0g (0.092 mola) to 500ml 1,4-dioxane, and melted 10.0g (0.096 mola) of sodium hydrogensulfates in 200ml water was added, and boiling reflux was carried out for three days. Generated precipitate was carried out the exception with the glass filter, and it washed by 50-degrees C 1,4-dioxane, it washed and dried by a small amount of water and tetrahydrofuran after that, and 52.5g (0.081 mola) of succinic-acid bis(2, 2, 3, 1, 4, 4, 5, and 5-octafluoro-1-pentyl)-2-sulfonic-acid sodium was obtained. 1 H-NMR(acetone- $\delta$ ): delta3.30 (d, 2H, and CH<sub>2</sub>CO), 4.53 (t, 2H, CHCO), 4.80 (t, 4H, CH<sub>2</sub>O), 7.72 (s, 2H, HC<sub>2</sub>F2).

[0180] Example 1 (polymerization example of a PTFE fine powder latex)

3.0g of surfactants of 120g (melting point of 58 degrees C) and formula-CF3CF2CF2OCF(CF3) CF2OCF(CF3) COONaH was taught to the autoclave with a support stirring screw made from the stainless steel of 6l inner capacity for 3l, of deionized water, and paraffin was, and as an initiator, ammonium persulfate (APS) was used up to so that it might become the concentration of 10 ppm to water. Having pressed fit until it became 0.88 MPa by the TFE monomer after the 2 times permutation by the TFE monomer, and maintaining stirring at 250rpm, after carrying out the nitrogen purge of the inside of an autoclave enough, it heated to 70 degrees C and the polymerization was started. Since the pressure in a polymerization system declined with advance of a polymerization, additional press fit of the TFE was carried out, and the polymerization pressure force was maintained at 0.78MPa(s). After polymerization initiation, when polymer polymerization \*\*\* was 10.5 mass %, 2 ppm of hydroquinone were added to water, and the polymerization was continued as it was. When polymer \*\*\* reached 24.5 mass %, TFE was emitted, the polymerization was suspended and the PTFE latex of this invention was obtained.

[0181] The number average particle diameter of the PTFE particle in this latex (primary particle) was 300nm.

[0182] After diluting the obtained PTFE latex with water to the solid content concentration 12 - 13 mass %, it stirred mechanically and condensed, and after recovery, it dried at 130 degrees C for 18 hours, and the PTFE fine powder of this invention was obtained (standard specific gravity: 2.17).

[0183] It mixed with the shaping assistant (PI1620 (trade name) made from Idemitsu Petrochemistry), this PTFE fine powder was pasted, and paste extrusion shaping was presented. Paste extrusion was performed the following condition.

Extruder: The autograph by Shimadzu Corp.

Reduction ratio (R/R): 100 [0184] it was 37MPa, when heating baking of the obtained extrusion-molding object was carried out for 5 minutes at 380 degrees C, it considered as mold goods and the tensile strength of this thing was investigated.

[0185] In addition, the measuring method of each physical properties is as follows.

Standard specific gravity: ASTM According to D 1457-69, it measures by the sinking method. A

2006/06/19

test portion fills up metal mold (25mm<sup>3</sup>) with 12g of fluorine polymer powder, and produces it by imposing the load of 20MPa and holding for 2 minutes.

The diameter of a primary particle of a fluorine polymer latex: The permeability of 550nm incident light [ as opposed to / dilute the fluorine polymer (PTFE) particle latex after an emulsion polymerization with water to solid content concentration 0.15 mass %, and / the unit length of these diluted aqueous dispersion liquid ]. The diameter of a primary particle is determined using the calibration curve which plotted and created the several set semi-diameter mean particle diameter which measured and determined unidirectional particle diameter from the transmission electron microscope photograph from the value of the above-mentioned permeability (550nm) measured about each sample.

Tensile strength of mold goods: JIS K 1 measures according to 5400.

[0181] A result is indicated to Table 1.

[0187] the surfactant of example 2 example 1 — formula: — it changed into H(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OC(CF<sub>3</sub>)<sub>3</sub> COONa, the charge and the polymerization formula were performed similarly, and the PTFE latex was obtained.

[0188] the surfactant of example 3 example 1 — formula: — it changed into HANOCO(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub> COONa, the charge and the polymerization formula were performed similarly, and the PTFE latex was obtained.

[0189] the surfactant of example 4 example 1 — formula: — it changed into H(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OCOC(CH<sub>3</sub>)<sub>2</sub>(SO<sub>3</sub>Na) CH<sub>2</sub>COOCH<sub>2</sub>CH<sub>2</sub>(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>, the charge and the polymerization formula were performed similarly, and the PTFE latex was obtained.

[0190]  
[Table 1]

図1: PTFEファインパウダーラテックスの重合実験例

	界面活性剤	温度 [°C]	一次粒子径 [nm]	ポリマー 比重	成層体の 引張り強度 [MPa]
実施例 1	C <sub>8</sub> F <sub>7</sub> -CF <sub>2</sub> Pd-CF(CF <sub>3</sub> ) <sub>2</sub> -CF <sub>2</sub> Pd-(CF <sub>3</sub> ) <sub>2</sub> COOEt <sub>n</sub>	70	300	2.17	37
実施例 2	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PCl-CH <sub>2</sub> Cl-Pd-(CF <sub>3</sub> ) <sub>2</sub> COOEt <sub>n</sub>	70	195	2.18	36
実施例 3	R-SnOC(CH <sub>3</sub> ) <sub>2</sub> CF <sub>2</sub> -Pd-	70	315	2.185	35.5
実施例 4	D-COOCC(CH <sub>3</sub> ) <sub>2</sub> Sn(R) <sub>2</sub> O-CH <sub>2</sub> OPd- R=CH <sub>3</sub> , CF <sub>3</sub> , Et	70	308	2.178	35.8

[0191] Example 5 (polymerization of a denaturation PTFE fine powder latex)

They are 3L of deionized water, and paraffin wax to the autoclave with a surface stirring aeroflo made from the stainless steel of 8L inner capacity. Having prepared 3.0g of support active agents of 100g (melting point of 56 degrees C), and formula: CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>OCF(CF<sub>3</sub>) CF<sub>2</sub>OCF(CF<sub>3</sub>) COONH<sub>4</sub>, and maintaining stirring at 280rpm, after nitrogen permeated the TFE monomer commutation twice 3 times, the pressure up of the inside of an autoclave was carried out to 0.58MPa(a) by the TFE monomer.

[0192] Next, the water solution which melted 0.3g (APS) of 11.25mg ammonium persulfates in 20 cc water continuously in perfluoro propyl vinyl ether (PPVE), and the water solution which melted 360mg disuccinic acid peroxide (DSP) are pressed fit by the TFE monomer, and autoclave internal pressure is set to 0.78MPa(a). Although a reaction advances accelerative, reaction temperature keeps 70 degrees C and agitating speed constant 280 rpm. A TFE monomer is continuously accelerated so that internal pressure may be maintained at 0.78MPa(a).

[0193] After adding an initiator, when the TFE monomer consumed at the reaction amounts to 1300g, supply and stirring of a TFE monomer are stopped. The gas in an autoclave is emitted until internal pressure is immediately set to 0.18MPa(a), it changes to Rhine of the mixed monomer of CTFE containing 1.5-mol % of CTFE subsequently prepared beforehand, and TFE, and continuation supply is carried out. That is, a mixed monomer is maintained to internal pressure 0.78MPa, stirring is maintained to 280rpm, and it reacts successfully.

2006/06/19

19/30 ページ

[0194] When the consumption of a mixed monomer amounts to 130g, supply and stirring of a mixed monomer are stopped, a monomer is emitted until the inside of an autoclave becomes ordinary pressure immediately, contents are taken out, and a reaction is ended.

[0195] When the gas chromatography analyzed the mixed gas under reaction by the mixed monomer (namely, stage of reaction of the shell of a particle), and in an autoclave, it was about 0.9-1.1-mol % the consumption of the TFE consumption per mixing monomer of the ezeene product. When the evaporation in this reaction is calculated, it will become 1300:130, 91:9 [i.e., ].

[0196] From the particle to dryness of a part of last latex was carried out and polymer density measurement of the solid content was carried out, it was 32 mass %. The mean particle diameter of a latex was 230nm.

[0197] It was 2.178, when coagulation desiccation of the obtained latex was carried out like the example 1 and specific gravity was measured. In addition, when PPVE and the CTFE content in a polymer were measured, they were 0.02 mass % and 0.09 mass %. The value to which the CTFE content multiplied the ratio of the absorbance of 2380cm<sup>-1</sup> to the absorbance of 957cm<sup>-1</sup> of an infrared-absorption spectral band by 0.56, and the PPVE content determined the value which multiplied the ratio of the absorbance of 995cm<sup>-1</sup> and 2380cm<sup>-1</sup> by 0.95 as the content in a polymer.

[0198] In addition, the measuring method of each physical properties is the same as the approach of example 1 publication.

Standard specific gravity: ASTM According to D 1457-89, it measures by the sinking method. A test portion fills up metal mold (25mm<sup>3</sup>) with 12g of fluorine polymer powder, and produces it by imposing the load of 20MPa and holding for 2 minutes.

The diameter of a primary particle of a fluorine polymer latex : The permeability of 550nm incident light ( as opposed to / dilute the fluorine polymer (PTE) particle latex after an emulsion polymerization with water to solid content concentration 0.15 mass % , and / the unit length of these diluted aqueous dispersion liquid ). The diameter of a primary particle is determined using the calibration curve which plotted and created the several set semi-diameter mean particle diameter which measured and determined unidirectional particle diameter from the transmission electron microscope photograph from the value of the above-mentioned permeability (550nm) measured about each sample.

Tensile strength of mold goods: JIS K It measures according to 5400.

[0199] the surfactant of example 6 example 5 — formula: — it changed into H(CF2CF2)2CH2CO2C(CF3) COONH4, and the polymerization was performed like the example 5 except having changed APS into 12.3mg and having changed polymerization temperature into 85 degrees C for the charge of DSP at 180mg.

[0200] the surfactant of example 7 example 5 — formula: — the polymerization was performed like the example 5 except having changed into HANOCO(CF2CF2)2COONH4.

[0201] the surfactant of example 8 example 5 — formula: — it changed into H(CF2CF2)2CH2CO2C(CH3O3Na) CH2COOCH2CF2CF2)2H, and the polymerization was performed like the example 5 except having changed APS into 12.3mg and having changed polymerization temperature into 85 degrees C for the charge of DSP at 180mg.

Table 21

表2: 変性PTFEファインパウダーラテックスの重合実験例

界面活性剤	温度 [°C]	DSP [m]	APS [mg]	一次粒子径 [nm]	ポリマー 収量	炭素体の 引張強度 [MPa]
実施例5 CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> COF (CF <sub>3</sub> ) <sub>2</sub> CO <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> COOH <sub>2</sub>	70	340	11.25	210	1.278	39
実施例6 昇(CF <sub>3</sub> CF <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> COOH <sub>2</sub>	85	180	7.3	275	2.18	38
実施例7 昇(CF <sub>3</sub> CF <sub>2</sub> ) <sub>2</sub> COOH <sub>2</sub>	70	340	11.25	300	2.19	36.6
実施例8 昇(CF <sub>3</sub> CF <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> COOCH <sub>3</sub> (50%)CH <sub>3</sub> CO <sub>2</sub> CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	85	180	17.3	280	2.162	3.7

20/30 ページ

[0203] Example 9 (preparation of PTFE and denaturation PTFE concentration dispersion)

To the PTFE dispersion liquid (polymer concentration: 24 mass %) obtained in the example 1, it is a nonionic surfactant. Addition of the C13H27O(C12H25CO) nH (n = 8.5, 49 degrees C of cloudy points) (Nippon Oil & Fats make; trade name DISU par Norianc TOC) is carried out 10% (solid content mass for a polymer); and the aqueous ammonia of sufficient amount to raise pH of dispersion liquid from about 3 to about 10 further is added. The obtained dispersion liquid are quietly stirred for several minutes, and it heats at 55 degrees C, and puts for 24 hours. Those with 65 mass % and its Despa Norianc TOC content of the solid content concentration of the concentration dispersion liquid which removed the produced transparent supernatant layer and were obtained were 3.5% on the basis of the mass of dispersion liquid. Despa Norianc TOC was further added about 2.5% on the basis of the mass of dispersion liquid, and about 60% of solid content and a surfactant content were made into about 6%.

[0204] To the PTFE dispersion liquid (polymer concentration: 24 mass %) obtained in the example 10 example 2, it is a nonionic surfactant. Addition of the C13H27O(C12H25CO) nH (n = 9.5, 58.8 degrees C of cloudy points) is carried out 10% (solid content mass for a polymer), and the aqueous ammonia of sufficient amount to raise pH of dispersion liquid from about 3 to about 10 further is added. The obtained dispersion liquid are quietly stirred for several minutes, and it heats at 70 degrees C, and puts for 24 hours. Those with 68 mass % and its Despa Norianc TOC content of the solid content concentration of the concentration dispersion liquid which removed the produced transparent supernatant layer and were obtained were 3.5% on the basis of the mass of dispersion liquid. Despa Norianc TOC was further added about 2.5% in ll. of samples of dispersion liquid, and about 60% of solid content and a surfactant content were made into those 6%.

[0205] Using the PTFE dispersion liquid obtained in the 11 to example 16 examples 3-8, it condensed by the same formula as an example 10, and concentration liquid as shown in Table 3 was obtained.

[0208] Like examples 9 and 10, it prepared so that the solid content concentration of a polymer might become about 6% about a surfactant content about 60%.

**[0207]**

[Table 3]

実施例	元のPTFE 分散剤	界面活性剤	炭化温度 [℃]	炭化後の ポリマー 濃度 [質量%]	炭化後のノニオン性 界面活性剤濃度 [質量%] 対ポリマー の相分量
実施例9	実施例2で存在	C <sub>12</sub> H <sub>25</sub> (C <sub>12</sub> H <sub>25</sub> のβ G=8.5, 熔点49℃)	55	83	1.4
実施例10	実施例2で存在	C <sub>12</sub> H <sub>25</sub> (C <sub>12</sub> H <sub>25</sub> のβ G=8.5, 熔点58.4℃)	70	84	1.5
実施例11	実施例3で存在	同上	70	67	2.3
実施例12	実施例4で存在	同上	70	65	2.8
実施例13	実施例5で存在	同上	70	70	2.1
実施例14	実施例6で存在	同上	70	71	2.9
実施例15	実施例7で存在	同上	70	69	3.1
実施例16	実施例8で存在	同上	70	68	2.2

[0208] Example 17 (manufacture of a non-fibril plasticity PTFE polymer particle)  
9.0g of surfactants of 3I, [ of deionized water ] and paraffin wax 120g (melting point of 56 degrees C) and formula:CF3CF2CF2OCF(CF3) CF2OCF(CF3) COONH4 was taught to the autoclave with a support stirring aerofoil made from the stainless steel of 6l. inner capacity. It heated to 70 degrees C, having pressed fit until it set after the 2 times permmutation by the TFE

2006/06/19

monomer and was set to 1.0MPa(s) by the TFE monomer, and maintaining stirring at 250rpm, after carrying out the nitrogen purge of the inside of an autoclave enough. As a chain transfer agent, by ordinary pressure, 40 cc water solution which melted 300mg (APS) of ammonium persulfates which are 15g perfluoro propyl vinyl ether (PPVE) and a polymerization initiator considering 130 cc ethane as a comonomer was prepared in the system, and the reaction was started. During the reaction, since the pressure in a polymerization system declined with advance of a polymerization, additional press fit of the TFE was carried out, and the polymerization pressure was maintained at 1.0(=0.05) MPa. After polymerization initiation, when TFE monomer consumption amounted to 530g, TFE supply and stirring were stopped, and the internal pressure of a tub was emitted to ordinary pressure, and the reaction was ended. Polymer solid content concentration was 15%. The number average particle diameter of the PTFE particle in this latex (primary particle) was 85nm.

[0209] The ammonium carbonate was added, it dried at 130 degrees C for 16 hours, and the obtained PTFE latex was made powdered, after carrying out condensation recovery. When paste extrusion was performed, the extrusion object is discontinuous and did not have the reinforcement according to fibrillation for whether it being  $\pi$ , and elongation.

[0210] After using this latex, adding Triton X-100 (made in Iom & Haas) about 6% to PTFE solid content as a nonionic surface active agent and aqueous ammonia's adjusting pH to 9, usable concentration PTFE dispersion was producible to the water repellent for cells by condensing so that moisture may be evaporated under reduced pressure and polymer solid content may become 60%. Particle diameter was 85nm before concentration.

[0211] The surfactant of 18 to example 17 was changed into the surfactant given in Table 4, the charge and the polymerization formula were performed similarly, and the PTFE latex was obtained. In addition, it checked that it could condense to 60% of polymer solid content concentration about the examples 18-20 as well as an example 17. The experimental result of examples 17-20 was collectively indicated to Table 4.

[0212]

[Table 4]

表 4 : 非フッ素系 PTFE 重合体分散液の製造実施例

	界面活性剤	温度(°C)	一次粒子径(nm)
実施例17	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> COONH <sub>4</sub>	70	85
実施例18	H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> COONH <sub>4</sub>	70	180
実施例19	H <sub>2</sub> COCH(CF <sub>2</sub> CF <sub>2</sub> )COONH <sub>4</sub>	70	110
実施例20	H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub> COCH(SO <sub>3</sub> Na)CH <sub>2</sub> COCH(SO <sub>3</sub> Na)CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub>	70	91

[0213] Example 21 (emulsion polymerization of FEP)

CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>COONH<sub>4</sub> was taught as 1500g of deionized water, and a surfactant, and 1000 ppm of ammonium carbonates were taught to the autoclave with an agitator made from the stainless steel of 3l inner capacity as 7500 ppm and a buffer for pH. After carrying out the nitrogen purge of the autoclave enough, it stirred by 600rpm and heated to 80 degrees C. Then, HFP gas and TFE gas were pressed fit and the gaseous layer section presentation was made into TFE/HFP=25/75-mol% by tub internal pressure 0.8MPaG. As an initiator, when ammonium persulfate (APS) was prepared so that it might become the concentration of 500 ppm, the polymerization reaction started it, and the fall of a pressure was seen. During the polymerization reaction, additional press fit of the TFE/HFP=91/9-mol % of mixed gas was carried out, and tub internal pressure 0.8MPaG was maintained. Moreover, since a reaction rate fell by decomposition reduction of an initiator, 200 ppm of APSs were added every 3 hours after reaction initiation, and the rate of polymerization was made to fixed-size, 20 hours after polymerization initiation, stirring was stopped, the polymerization was suspended, the TFE/HFP gas in a tub was emitted, and it cooled to the room temperature.

[0214] The solid content concentration of the FEP latex of obtained this invention was 20.5

mass %, and the number average particle diameter of a primary particle was 180nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was FEP of HFP12.3 mass % and the melt flow values in 372 degree C and 5kg load were 0.0056 ml/sec.

[0215] Example 22 (emulsion polymerization of FEP)

HCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>COCH(SO<sub>3</sub>Na)CH<sub>2</sub>COCH(SO<sub>3</sub>Na)CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub> was used as a surfactant, and also the same actuation as an example 21 was performed, and the emulsion polymerization of FEP was performed.

[0216] The solid content concentration of the FEP latex of obtained this invention was 19.5 mass %, and the number average particle diameter of a primary particle was 190nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was FEP of HFP12.1 mass % and the melt flow values in 372 degree C and 5kg load were 0.0062 ml/sec.

[0217] Example 23 (emulsion polymerization of FEP)

HANOCO(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>COONH<sub>4</sub> was used as a surfactant, and also the same actuation as an example 21 was performed, and the emulsion polymerization of FEP was performed.

[0218] The solid content concentration of the FEP latex of obtained this invention was 18.8 mass %, and the number average particle diameter of a primary particle was 210nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was FEP of HFP11.7 mass % and the melt flow values in 372 degree C and 5kg load were 0.0047 ml/sec.

[0219] Example 24 (emulsion polymerization of FEP)

HCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>COCH(SO<sub>3</sub>Na)CH<sub>2</sub>COCH(SO<sub>3</sub>Na)CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub> were used as a surfactant, and also the same actuation as an example 21 was performed, and the emulsion polymerization of FEP was performed.

[0220] The solid content concentration of the FEP latex of obtained this invention was 18.3 mass %, and the number average particle diameter of a primary particle was 205nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was FEP of HFP11.5 mass % and the melt flow values in 372 degree C and 5kg load were 0.0051 ml/sec.

[0221] The experimental result of examples 21-24 was collectively indicated to Table 5.

[Table 5]

表 5

	乳化剤	ラテックス		最新ポリマー	
		固相分濃度(質量%)	一次平均粒子径(nm)	PPVE含有率(質量%)	メルトフロー値(372°C, 5kg荷重)(ml/sec)
実施例21	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> COONH <sub>4</sub>	20.5	180	12.3	0.0056
実施例22	H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> COONH <sub>4</sub>	19.5	190	12.1	0.0062
実施例23	H <sub>2</sub> COCH(CF <sub>2</sub> CF <sub>2</sub> )COONH <sub>4</sub>	18.8	210	11.7	0.0047
実施例24	H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CF <sub>2</sub> COCH(SO <sub>3</sub> Na)CH <sub>2</sub> COCH(SO <sub>3</sub> Na)CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub>	18.3	205	11.5	0.0051

[0223] Example 25 (emulsion polymerization of PFA)

5000 ppm of CF<sub>3</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>COONH<sub>4</sub> were taught to the autoclave with an agitator made from the stainless steel of 6l inner capacity as 3000g of deionized water, and a surfactant. After carrying out the nitrogen purge of the autoclave enough, ethane 20ml (under 25-degree-C atmospheric pressure) was taught as a chain transfer agent under the vacuum, and it stirred by 300rpm and heated to 70 degrees C. Then, perfluoro propyl vinyl ether (PPVE) 45g was added, TFE gas was pressed further fit, and tub internal pressure was set to 0.8MPaG(s). As an initiator, when ammonium persulfate (APS) was prepared so that it might become the concentration of 20 ppm, the polymerization reaction started it, and the fall of a pressure was

http://www4.ipdl.ncipi.go.jp/cgi-bin/ran\_web.cgi.ejje

2006/06/19

http://www4.ipdl.ncipi.go.jp/cgi-bin/ran\_web.cgi.ejje

2006/06/19

seen. During the polymerization reaction, additional press fit of the TFE gas was carried out, and tub internal pressure 0.8MPaG was maintained. 5 hours after polymerization initiation, stirring was stopped, the polymerization was suspended, the TFE gas in a tub was emitted, and it cooled to the room temperature.

[0224] The solid content concentration of the PFA latex of obtained this invention was 11.0 mass %, and the number average particle diameter of a primary particle was 131nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was PFA of PPVE5.5 mass % and the melt flow values in 372 degree C and 5kg load were 0.019 ml/sec.

[0225] Example 26 (emulsion polymerization of PFA)

H(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>COCH(SO<sub>3</sub>Na)CH<sub>2</sub>COCH(SO<sub>3</sub>Na)CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub> was used as a surfactant, and also the same actuation as an example 25 was performed, and the emulsion polymerization of PFA was performed.

[0226] The solid content concentration of the PFA latex of obtained this invention was 12.0 mass %, and the number average particle diameter of a primary particle was 129nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was PFA of PPVE5.8 mass % and the melt flow values in 372 degree C and 5kg load were 0.022 ml/sec.

[0227] Example 27 (emulsion polymerization of PFA)

HANOCO(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>COONH<sub>4</sub> was used as a surfactant, and also the same actuation as an example 25 was performed, and the emulsion polymerization of PFA was performed.

[0228] The solid content concentration of the PFA latex of obtained this invention was 11.5 mass %, and the number average particle diameter of a primary particle was 135nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was PFA of PPVE5.7 mass % and the melt flow values in 372 degree C and 5kg load were 0.017 ml/sec.

[0229] Example 28 (emulsion polymerization of PFA)

H(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>COCH(SO<sub>3</sub>Na)CH<sub>2</sub>COCH(SO<sub>3</sub>Na)CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub> were used as a surfactant, and also the same actuation as an example 25 was performed, and the emulsion polymerization of PFA was performed.

[0230] The solid content concentration of the PFA latex of obtained this invention was 11.5 mass %, and the number average particle diameter of a primary particle was 125nm. Moreover, when the white polymer obtained by coagulating this latex using a nitric acid was analyzed, it was PFA of PPVE5.8 mass % and the melt flow values in 372 degree C and 5kg load were 0.025 ml/sec.

[0231] The experimental result of examples 25-28 was collectively indicated to Table 6.

[Table 6]

[Table 6]

表 6

		ラテックス		最新ポリマー	
		固相分濃度 (質量%)	一次平均 粒子径 (nm)	PPVE含有率 (質量%)	メルトフロー値 372°C, 5kg荷重 (ml/sec)
実施例25	$\text{CF}_3\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{COONH}_4$	11.0	131	5.5	0.019
実施例26	$\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OCF}(\text{CF}_3)\text{COONH}_4$	12.0	129	5.8	0.022
実施例27	$\text{H}_2\text{NCOCH}_2\text{OCF}_2\text{CF}_2\text{COONH}_4$	11.5	135	5.7	0.017
実施例28	$\text{H}(\text{CF}_2\text{CF}_2)_2\text{CH}_2\text{OCOC}(\text{SO}_3\text{Na})\text{CH}_2\text{OCOC}(\text{SO}_3\text{Na})\text{CF}_2\text{CF}_2\text{CF}_2$	11.5	125	5.8	0.025

[0233] Example 29 (emulsion polymerization of PVdF)

After it taught 45ml of ion exchange water, and 0.25g of emulsifiers to the autoclave made from stainless steel of 100ml content volume and nitrogen permuted with it enough, VdF4.8g was taught by the vacuo. The autoclave was put into the 70-degree C constant temperature bath shaker, and it shook until the pressure was fixed (2.8MPaG). When the pressure became fixed,

the APS1.0 mass % water solution was prepared with 5.0g plunger pump, and the reaction was started. The reaction was performed at 70 degrees C for 2.5 hours.

[0234] The residual monomer was emitted into atmospheric air after reaction termination, and emulsified liquid was obtained. Moreover, the average rate of polymerization was 32.2 g/hr/liter-water. Some emulsified liquid was taken, with the Microtrac UPA particle-size measuring device made from Honeywell, mean particle diameter was measured and the particle number was computed from the value.

[0235] Examples 30-33 (emulsion polymerization of PVdF)

Except having changed the emulsifier into various kinds, it is making it react like an example 29, and emulsified liquid was obtained, respectively. The result was summarized in Table 7.

[0236] Except having changed example of comparison 1 emulsifier into (CF<sub>2</sub>)<sub>2</sub>COONH<sub>4</sub>, it is making it react like an example 29, and emulsified liquid was obtained. The result was summarized in Table 7.

[0237]

[Table 7]

表 7 : P V d F の乳化剤の実施例と比較例

	乳化剤	乳化剤仕込量(g)	乳化剤濃度(mol/L-水)	混合濃度(g/L-水/tz)	粒子径(μm)	粒子数(×10 <sup>13</sup> /ml-水)
実施例29	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> COONH <sub>4</sub>	0.25	0.012	47.2	96	194
実施例30	CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> COONH <sub>4</sub>	0.25	0.012	35.3	180	17.8
実施例31	H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> COCH(SO <sub>3</sub> Na)CH <sub>2</sub> COCH(SO <sub>3</sub> Na)CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub>	0.23	0.012	25.8	253	4.10
実施例32	H <sub>2</sub> COCH(CF <sub>2</sub> CF <sub>2</sub> )COONH <sub>4</sub>	0.18	0.012	19.2	305	1.88
実施例33	H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> COCH(SO <sub>3</sub> Na)CH <sub>2</sub> COCH(SO <sub>3</sub> Na)CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub>	0.26	0.012	23.6	106	48.8
比較例1	F(CF <sub>2</sub> ) <sub>2</sub> COONH <sub>4</sub>	0.25	0.012	32.2	110	55.8

[0238] Example 34 (VdF/HFP copolymerization)

After it taught 45ml of ion exchange water, and 2.8g of emulsifiers to the autoclave made from stainless steel of 100ml content volume and nitrogen permuted with it enough, 4.9g was taught for VdF/HFP mixed gas (40 / 80 mole ratios) by the vacuo. The autoclave was put into the 80-degree C constant temperature bath shaker, and it shook until the pressure was fixed (1.31MPaG). When the pressure became fixed, the APS 0.5 mass % water solution was prepared with 5.0g plunger pump, and the reaction was started. The reaction was performed at 80 degrees C for 0.5 hours.

[0239] The residual monomer was emitted into atmospheric air after reaction termination, and the diameter[ of a large drop ]-ized latex was obtained. Moreover, the average rate of polymerization was 104.4 g/hr/liter-water.

[0240] Since the particle diameter of the generated latex particle was small, when it was not able to measure directly, it measured, after carrying out the polymerization of the particle further and enlarging particle diameter. The procedure is explained below.

[0241] After taking a part of generated latex, teaching what was diluted with ion exchange water 10 to 100 times to the autoclave of 100ml content volume and nitrogen's permuting enough, VdF 2.8g was taught by the vacuo.

[0242] The autoclave was put into the 80-degree C constant temperature bath shaker, and it shook until the pressure was fixed (2.40MPaG). When the pressure became fixed, 5.0g preparation reaction was started for the APS 1.0 mass % water solution with the plunger pump. The reaction was performed at 80 degrees C for 0.5 hours.

[0243] The residual monomer was emitted into atmospheric air after reaction termination, and the diameter[ of a large drop ]-ized latex was obtained. A part of this is taken and it is Microtrac UPA made from Honeywell. Mean particle diameter was measured with the particle-size

